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FINAL REPORT: POLYANILINE MEMBRANES FOR SEPARATION APPLICATIONS

by

Richard B. Kaner

University of California, Los Angeles
Department of Chemistry and Biochemistry
405 Hilgard Avenue
Los Angeles, CA 90095-1569

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Richard B. Kaner

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, Los Angeles
Department of Chemistry and Biochemistry
405 Hilgard Avenue
Los Angeles, CA 90095-1569

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13. ABSTRACT *(Maximum 200 words)*
High quality membranes of polyaniline/ethylaniline copolymers along with polyaniline/polyimide blends have been synthesized. Water permeates preferentially over organics (such as acetic acid) through doped polyaniline due to a combination of favorable diffusion and solubility. Fully doped polyaniline is among the most selective membranes yet developed for water/acetic acid separations: e.g. at 50% water/50% acetic acid the selectivity α is > 1,000. Fully doped polyaniline membranes are highly selective effectively blocking species with diameters $\geq$ 4.5 Å. In addition to traditional dopants, ion implantation has been found to be an effective method to produce very highly conductive polyaniline films which exhibit metallic-like behavior.

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Objective and Approach:

A comprehensive study of dopable conjugated polymers as permselective membranes has been carried out. This work focused on the effects of dopants on the membranes' permeability and selectivity. Pervaporation, a process in which one component is separated from a mixture of liquids by selective transport through a membrane, will benefit from the ability to tailor a membrane's properties after formation; i.e. for polyaniline membranes, through the doping process using common acids and bases. Polyaniline is a model conjugated polymer because of its processibility, simple acid/base doping chemistry and air and thermal stability. Polyaniline membranes were first studied for individual solvent's permeation to gain fundamental information. Then mixtures, such as of several organic acids and water, were investigated. The effects of size and concentration of permeating acids on polyaniline films were examined. Further investigations involved separation of other organic/water mixtures and the effects of modified polyaniline membranes on pervaporation. These new membranes involved the synthesis of copolymers and blends of polyaniline. Increases in flux through polyaniline films are now being explored through increasing the operating temperature and by developing asymmetric hollow fiber membranes.

Conclusions

High quality membranes of polyaniline and polyaniline/ethylaniline copolymers along with polyaniline/polyimide blends have been synthesized. Water permeates preferentially over organics (such as acetic acid) through doped polyaniline due to a combination of favorable diffusion and solubility. Fully doped polyaniline is among the most selective membranes yet developed for water/acetic acid separations: e.g. at 50% water/50% acetic acid the selectivity α is >1000. Fully doped polyaniline membranes are highly selective effectively blocking species with diameters ≥ 4.5Å. In addition to traditional dopants, ion implantation has been found to be an effective method to produce very highly conductive polyaniline films which exhibit metallic-like behavior.

Students Supported by ONR:

Graduate Students:

1. Jeannine A. Conklin* (Ph.D. awarded 10/94)
2. Shu-Chuan Huang*,+ (Ph.D. awarded 1/95)
3. Tim S. Su+ (Ph.D. awarded 7/96)
4. Ian Ball
5. Rhonda Larson*

Postdoctoral Associates:

1. Dr. Shu-Chuan Huang*,+

Undergraduates:

1. Song Nguyen*,+
2. Angela Kwon*,+
3. David K. Kim+
4. Belinda Lew*,+
5. Steve Luboviski
6. Annise Berger*
7. Kim Miller*,+
8. Jim Shimano+

* = female; + = Asian

Publication Highlights:

1. *Macromolecules*, **28**, 6522 (1995).
Block copolymers of aniline with ethylaniline have been synthesized and grown as high quality, free-standing films. The materials are thermally stable to above 400°C. The reactivity ratios for aniline and o-ethylaniline were determined to be 0.128 and 11.7, respectively. This results in long blocks of o-ethylaniline and short blocks of aniline. The greater the ethylaniline content of the copolymer, the higher the solubility in non-aqueous solvents. For example, whereas only 0.002g of pure polyaniline dissolved (technically dispersed) in 10 ml of tetrahydrofuran, with 47% and 84% ethylaniline, 0.048 g and ≥ 0.250 g of copolymer dissolved.

2. *Phys. Rev. B*, **54**, 11638 (1996).
In this paper, argon ions are implanted into high quality, free-standing polyaniline films. The resulting Ar^+ doped gold colored polymer has a conductivity of $800\Omega^{-1}cm^{-1}$, the highest room temperature conductivity reported so far. On cooling to 8K, this material shows metallic conductivity, a property not found in conventionally doped polyaniline which generally looks like a dirty metal. The metallic conductivity can be altered in a magnetic field of ≥2.7 Tesla. This work included a collaboration with the Naval Research Laboratory (see transition).

3. *Handbook of Conducting Polymers*, 2nd Edition (Dekker, 1997), pp. 945-961.
This chapter describes in detail how high quality free-standing polyaniline membranes can be used for liquid and gas separations. Separation of water from organic mixtures using fully doped polyaniline membranes is demonstrated. Doped polyaniline has a remarkable ability to exclude organics with sizes ≥ 4.5Å.

Presentation Highlights:
The first invitation to present our research on liquid separations using conjugated polymer membranes, at the 209th National Meeting of the American Chemical Society was likely the most memorable. A special symposium was devoted to applications of conjugated polymers and many colleagues in the field were impressed by the stability and possibilities for liquid separations using doped polyaniline membranes.

Award Highlights:
Belinda Lew, an undergraduate, was a Waldo Semon Research Award Finalist in Polymer Chemistry for her work on polyaniline membranes. She gave a presentation on her research and received the award at the University of Akron in Akron, Ohio. Belinda also earned the UCLA Ethel Terry McCoy Prize for excellence in Chemistry and graduated Phi Betal Kappa with Highest Honors. She is now a graduate student in chemistry at Harvard University.

Richard Kaner, the P.I., received a 1996-97 John Simon Guggenheim Foundation Fellowship for "distinguished achievement in the past and exceptional promise for future accomplishment." He was among the 158 scientists and artists chosen from 2,791 nominees.

Transition:
In the course of studying the effects on permeability through conjugated polymer membranes by changing dopants, the idea occurred to us of using ion implantation as the ultimate method of forming modified thin asymmetric membranes. Although the effects on permeability were modest, we did succeed in making the most highly conducting polyaniline films known to date with a room temperature conductivity of 800 $\Omega^{-1}cm^{-1}$ (*Mat. Res. Soc. Symp. Proc.*, **413**, 609, 1996). These materials were among the first polyanilines to show metallic-like conductivity at low temperatures (300K-1.8K) (*Phys. Rev. B*, **54**, 11638, 1996). This work was carried out in collaboration with coworkers at the U.S. Naval Research Laboratory and at the A.F. Joffe Physico-Technicial Institute in St. Petersburg, Russia.

Richard B. Kaner

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